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On the weighting of reflexions in least-squares calculation of non-cubic unit-cell dimensions.

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It is well known that extrapolation for non-cubic cell dimensions inherently requires that weight be allocated to individual *hkl* reflexions in accordance with the particular parameter being determined. This is usually practised to some extent in graphical extrapolation but not in the more sophisticated 'least-squares' techniques developed by Cohen (1935), Hess (1951) and others. Hess has made provision in the 'least-squares normal equations' to include a weighting term W, which is the product of two factors, $W(\theta)$ and $W(s)$. These respectively take into account the influence of Bragg angle θ and the accuracy of the linear film distances s upon the ultimate precision of cell dimensions.

With the advent of high-speed computers the objection to lengthy computations associated with the analytical procedures no longer arises. It is therefore little extra trouble to incorporate a third weight factor $W(hkl)$ into W, which facilitates h, k, l weighting. In establishing such a factor it is desirable that certain boundary conditions be satisfied. For instance, consider the following expression for hexagonal cells, the terms retaining their conventional meaning:

$$4 \sin^2 \theta/\lambda^2 = 4(h^2+hk+k^2)/3a^2 + l^2/c^2.$$

$hk0$ lines render a exempt from any error in the term containing c whereas $00l$ lines are completely independent of a. This implies $W_a(hk0) = 1$, $W_a(00l) = 0$.

The following is the simplest expression which complies with the two above extreme specifications and is adaptable to the general hkl reflexion:

$$W_a(hkl) = \frac{4(h^2+hk+k^2)/3a^2}{4(h^2+hk+k^2)/3a^2 + l^2/c^2}.$$

a is then determined by solving the 'normal equations' weighted with $W = W(s).W(\theta).W_a(hkl)$. Parameter c is obtained similarly. It will be noted that at least a crude approximation to c/a is presupposed.

Table 1. *Cell parameters a and c of* β-AgI, *with standard error, using various W functions*

Film	Cohen (Å)	Hess (Å)	Modified (Å)
1	4·59085 ± 0·00056	4·59063 ± 0·00039	4·59059 ± 0·00038
	7·50358 ± 0·00092	7·50363 ± 0·00064	7·50281 ± 0·00105
2	4·59217 ± 0·00031	4·59196 ± 0·00025	4·59190 ± 0·00021
	7·50764 ± 0·00051	7·50789 ± 0·00041	7·50818 ± 0·00059
3	4·59400 ± 0·00029	4·59381 ± 0·00016	4·59376 ± 0·00014
	7·50894 ± 0·00048	7·50943 ± 0·00027	7·50912 ± 0·00036
4	4·59341 ± 0·00041	4·59346 ± 0·00022	4·59346 ± 0·00022
	7·51153 ± 0·00068	7·51192 ± 0·00037	7·51261 ± 0·00036
5	4·59415 ± 0·00042	4·59415 ± 0·00030	4·59405 ± 0·00033
	7·51079 ± 0·00069	7·51096 ± 0·00049	7·51086 ± 0·00033
6	4·59371 ± 0·00026	4·59355 ± 0·00015	4·59355 ± 0·00012
	7·51320 ± 0·00042	7·51325 ± 0·00024	7·51448 ± 0·00041
7	4·59326 ± 0·00022	4·59324 ± 0·00014	4·59324 ± 0·00013
	7·51160 ± 0·00036	7·51195 ± 0·00024	7·51279 ± 0·00039
8	4·59311 ± 0·00023	4·59327 ± 0·00014	4·59329 ± 0·00012
	7·51033 ± 0·00038	7·51000 ± 0·00022	7·50960 ± 0·00027
9	4·59420 ± 0·00034	4·59401 ± 0·00020	4·59398 ± 0·00019
	7·51150 ± 0·00055	7·51181 ± 0·00033	7·51229 ± 0·00049
10	4·59357 ± 0·00045	4·59340 ± 0·00023	4·59337 ± 0·00017
	7·50924 ± 0·00074	7·50947 ± 0·00039	7·51008 ± 0·00072

As a test of the function W, data from ten powder photographs of hexagonal β-AgI, taken at temperatures ranging from 30 °C to 150 °C, were in turn subjected to the Cohen, Hess and modified weighting procedures, extrapolating against the Nelson–Riley function and setting $W(s) = 1$ for all lines. The problem was coded in FORTRAN II language for solution on an IBM 1620 computer. Results are illustrated in Table 1. Although the Hess method yields consistently smaller standard errors than does that of Cohen, there is no further significant overall reduction resulting from the modified scheme. However, an unsatisfactory feature of the Cohen and Hess methods, the identity of the relative errors in both a and c, does not arise with the modified procedure. In the exposures tested there were no $00l$ lines and an average of only 5 observations in about 20 were more favourable to a c extrapolation. Furthermore, these were generally found to be faint and therefore of comparatively poorer quality. It is to be expected that the relative error in c will exceed that in a, as is indeed reflected by the trend of the standard errors listed in Table 1.

The various weighting systems may be examined for sensitivity by removing (*a*) $hk0$ reflexions (average of 5 per film) or (*b*) all reflexions favouring c extrapolation. It would be desirable that situation (*a*) have no effect on parameter c and (*b*) very little effect on a. Table 2 summarizes the result of such an analysis with the Hess and Modified systems.

Table 2. *Results of sensitivity test*

	Average change in c as a result of (*a*)	Average change in a as a result of (*b*)
Hess	0·00061 Å	0·00006 Å
Modified	zero	0·00003

The latter is found to be more insensitive to the absence of reflexions unfavourable to extrapolation for a particular cell dimension.

The above proposed weighting system is readily applicable to orthorhombic and higher-symmetry crystals, which comprise the practical limit for powder X-ray diffraction. Extension to lower symmetries in which the angles become variables is difficult owing to the appearance of cross terms in the expression for cell parameters.

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